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(54) Recovering Non-Ferrous Metals

(57) At least one non-ferrous metal soluble in sulphuric acid is recovered from a strong sulphuric acid solution containing said metal and iron as sulphates by:

subjecting said solution in a subdivided form to thermal decomposition in a fluidized bed reactor at a temperature of from 600 to 750°C with 20—150% excess air for an average retention time of 1—12 hours to obtain calcine containing ferric oxide and the sulphate of said non-ferrous metal;

leaching said non-ferrous metal sulphate out from said calcine with water or dilute sulphuric acid solutions;

separating said leach solution containing said non-ferrous metal sulphate from the residue; and
recovering said non-ferrous metal from said leach solution, via electrolysis or any other method.

In a further embodiment the non-ferrous metal is recovered from a solid material containing the non-porous metal and iron by:

(a) roasting the material in a fluidised bed under the same temperature, air, and retention time conditions as above resulting in an atmosphere comprising SO₂, SO₃, H₂O and remaining O₂ and N₂ from the air to obtain a calcine containing ferrite and sulphates, oxysulphates and oxides of said non-ferrous metal, plus hematite,

(b) leaching the calcine with water or dilute sulphuric acid so that the sulphates, oxysulphates, and oxides of the non-ferrous metals are leached out in part from the calcine into the water or dilute H₂SO₄,

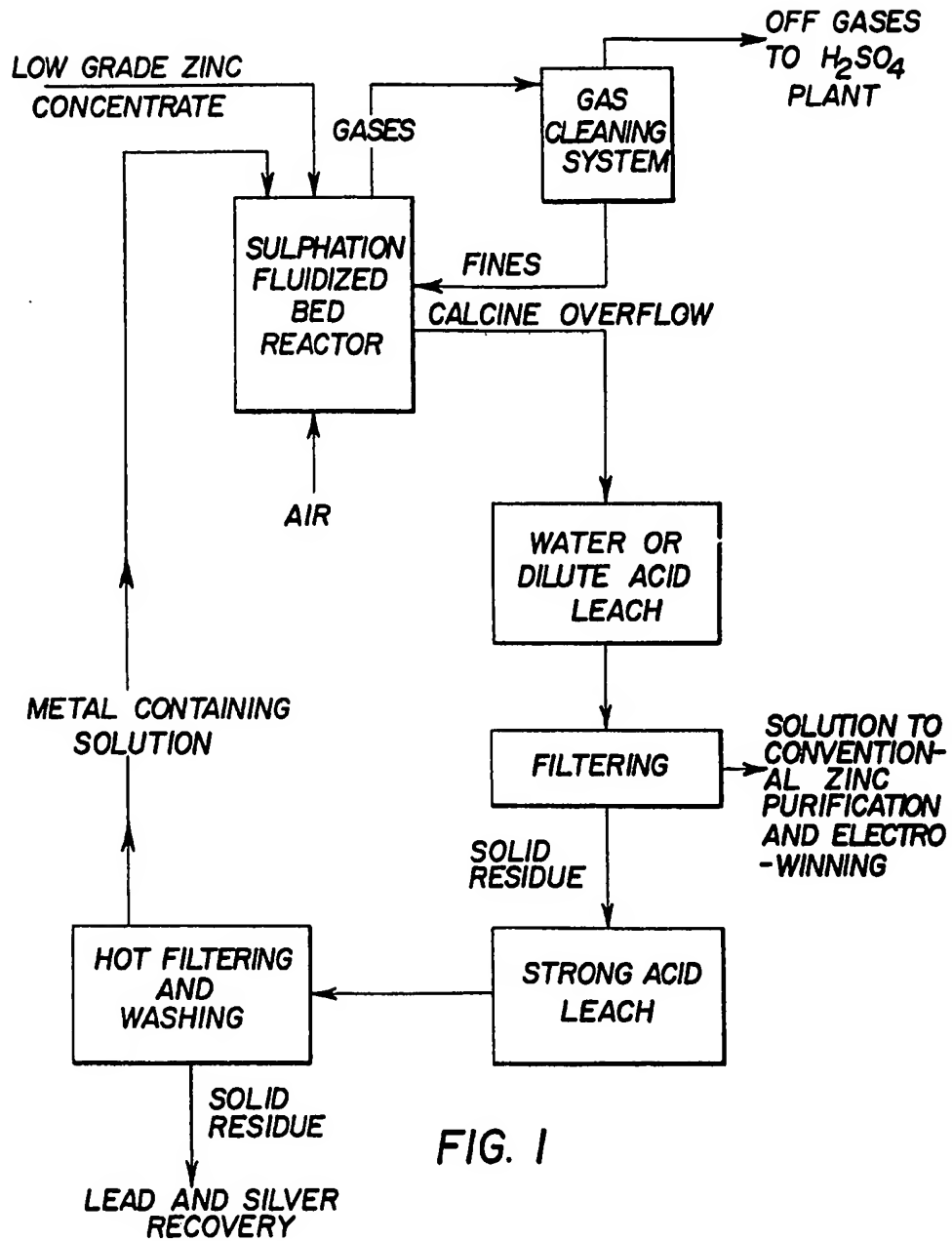
(c) subjecting the resulting each pulp to a liquid-solid separation

(d) leaching the solid residue of (c) with strong sulphuric acid solution such that the ferrite and unreacted sulphides of the non-ferrous are converted to sulphates

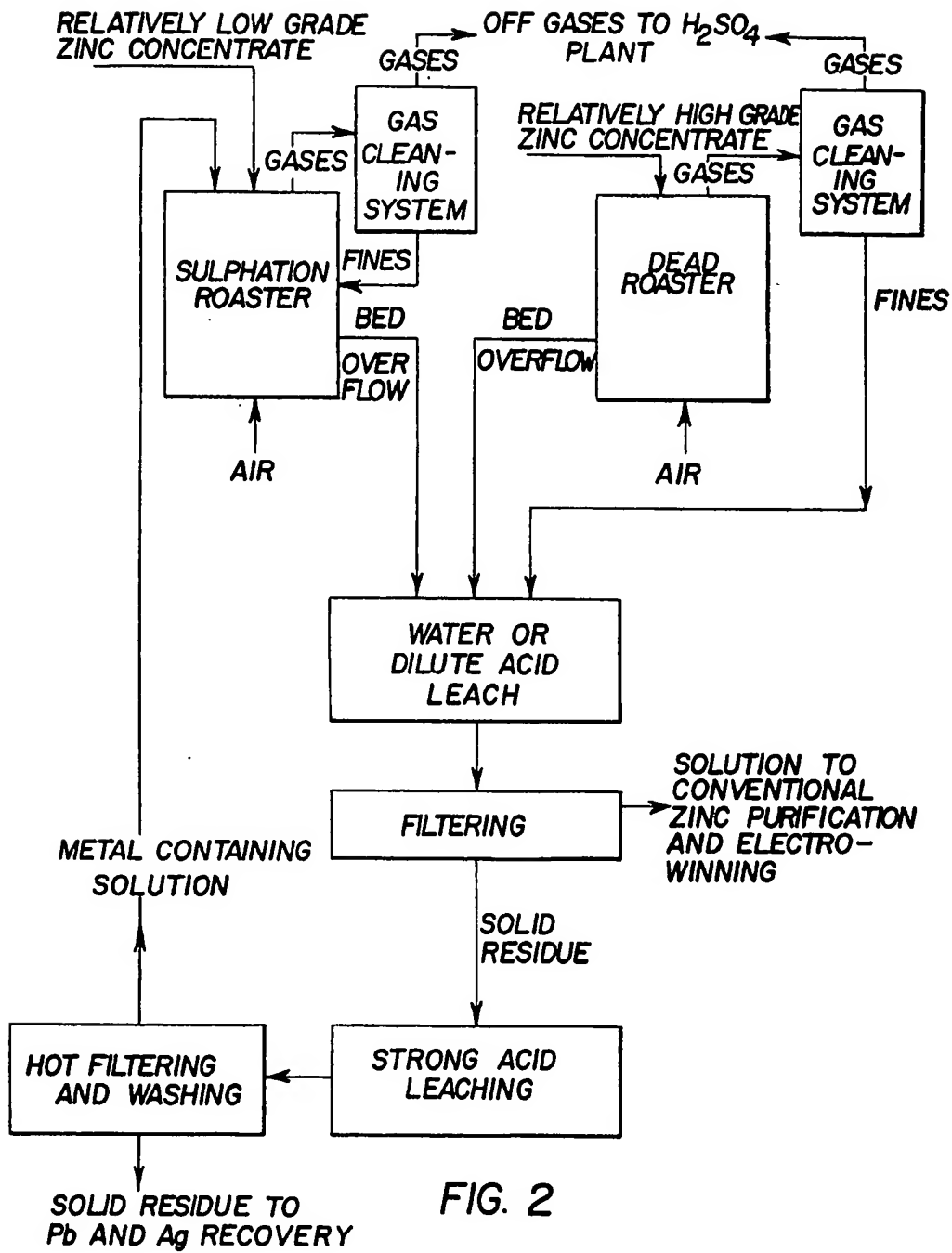
(e) subjecting the leach pulp from (d) to a liquid-solid separation

(f) recycling solution obtained in (e) to the fluidised reactor in a subdivided form to convert the sulphates of iron to ferric oxide, SO₂ and SO₃ and sulphuric acid to SO₂, SO₃ and H₂O.

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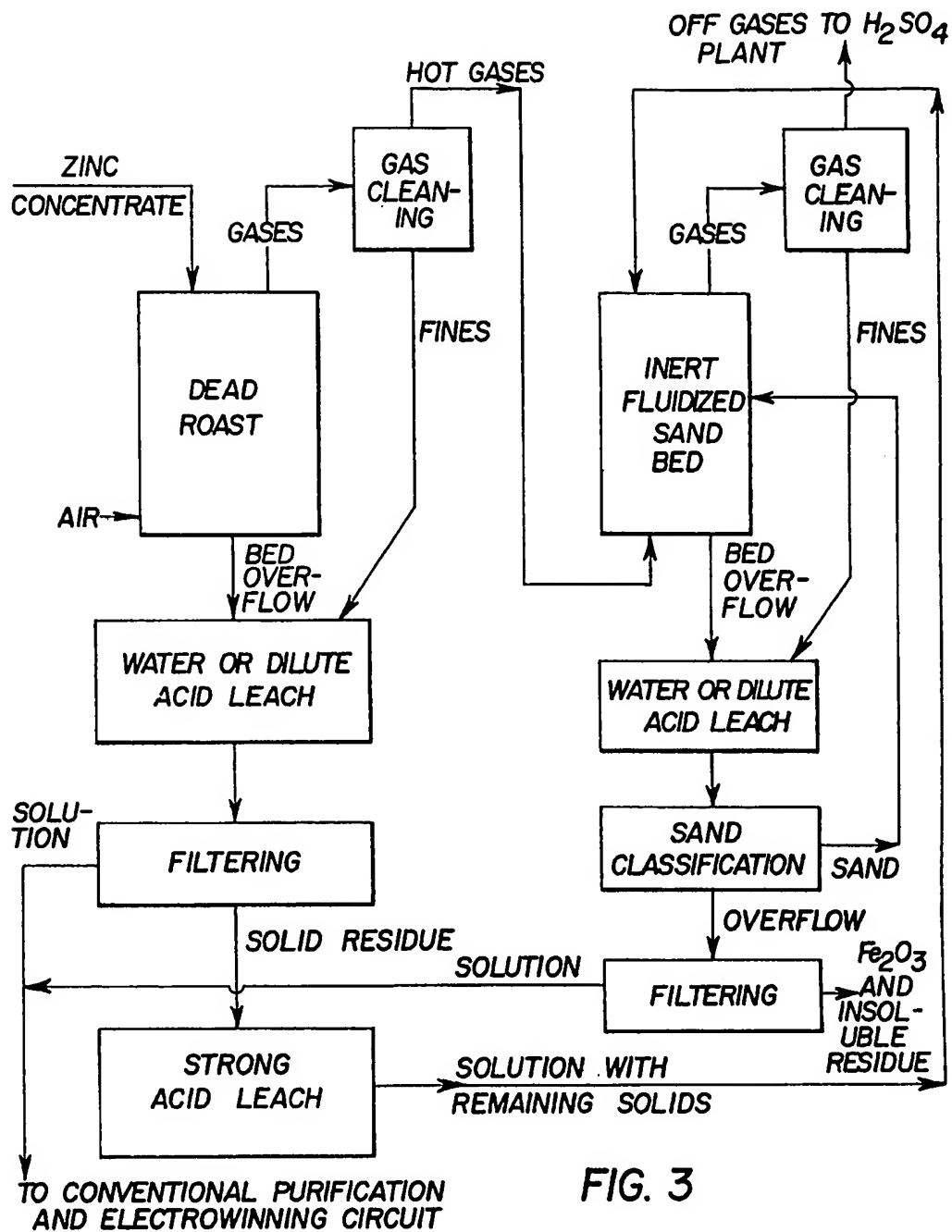


FIG. 3

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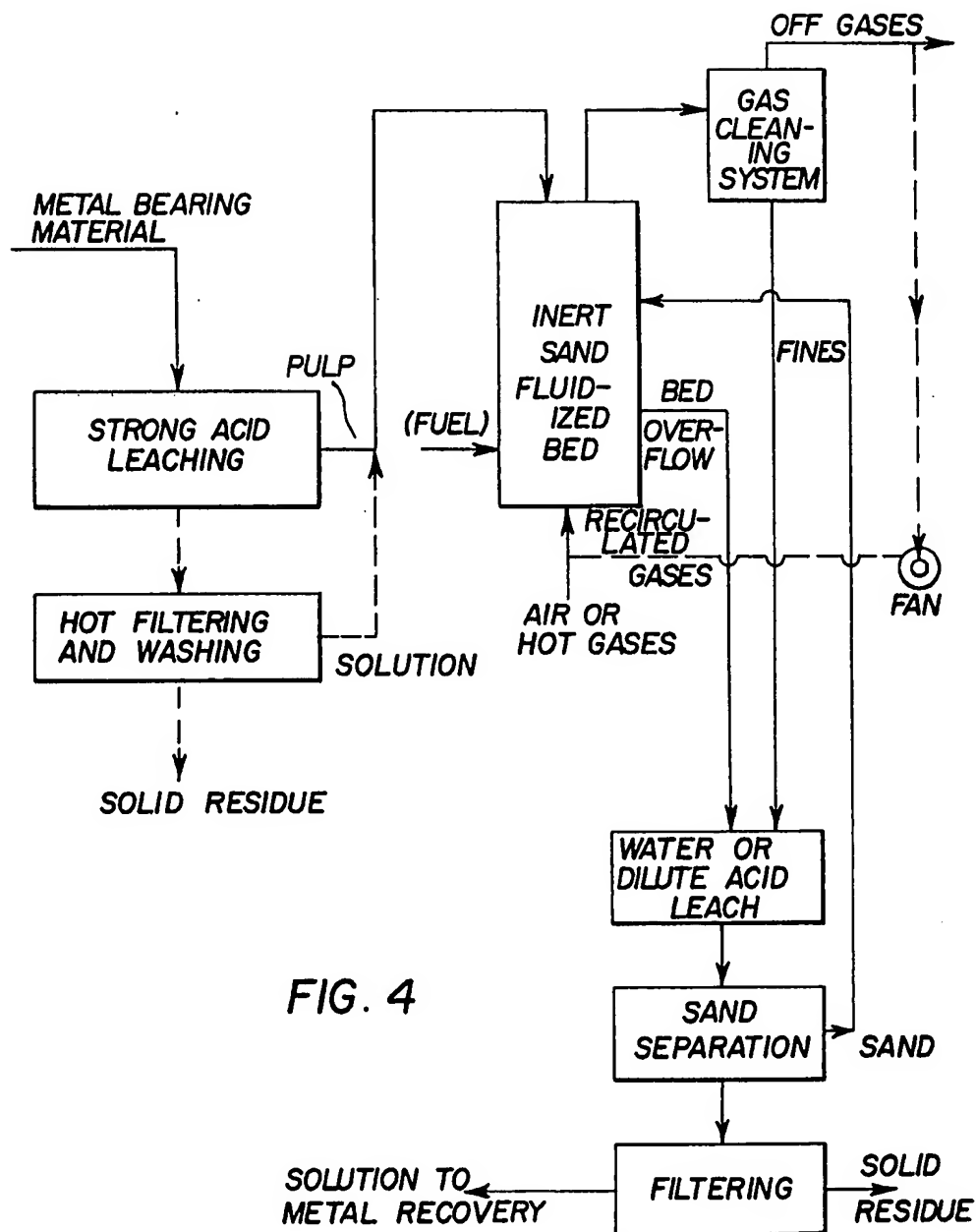
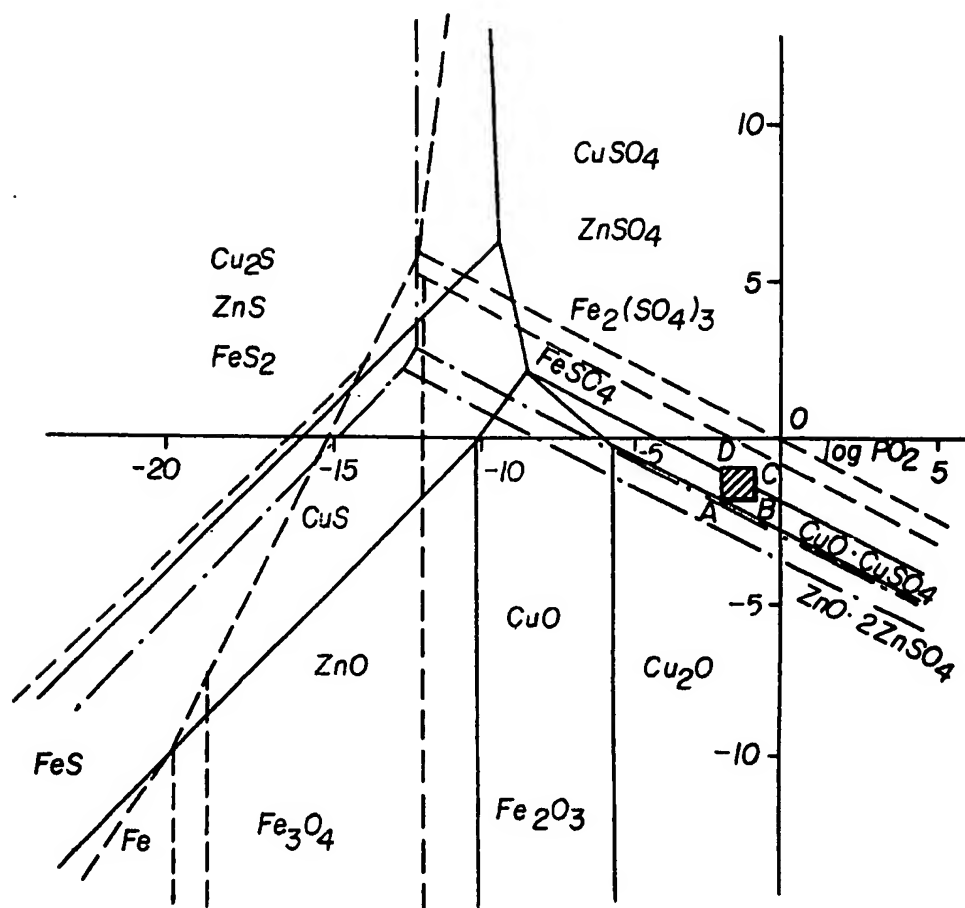


FIG. 4



STABILITY PHASE DIAGRAM

Zn-S-O SYSTEM

Cu-S-O SYSTEM

Fe-S-O SYSTEM

$T = 685^\circ\text{C}$ TOTAL PRESSURE = 1 Atm

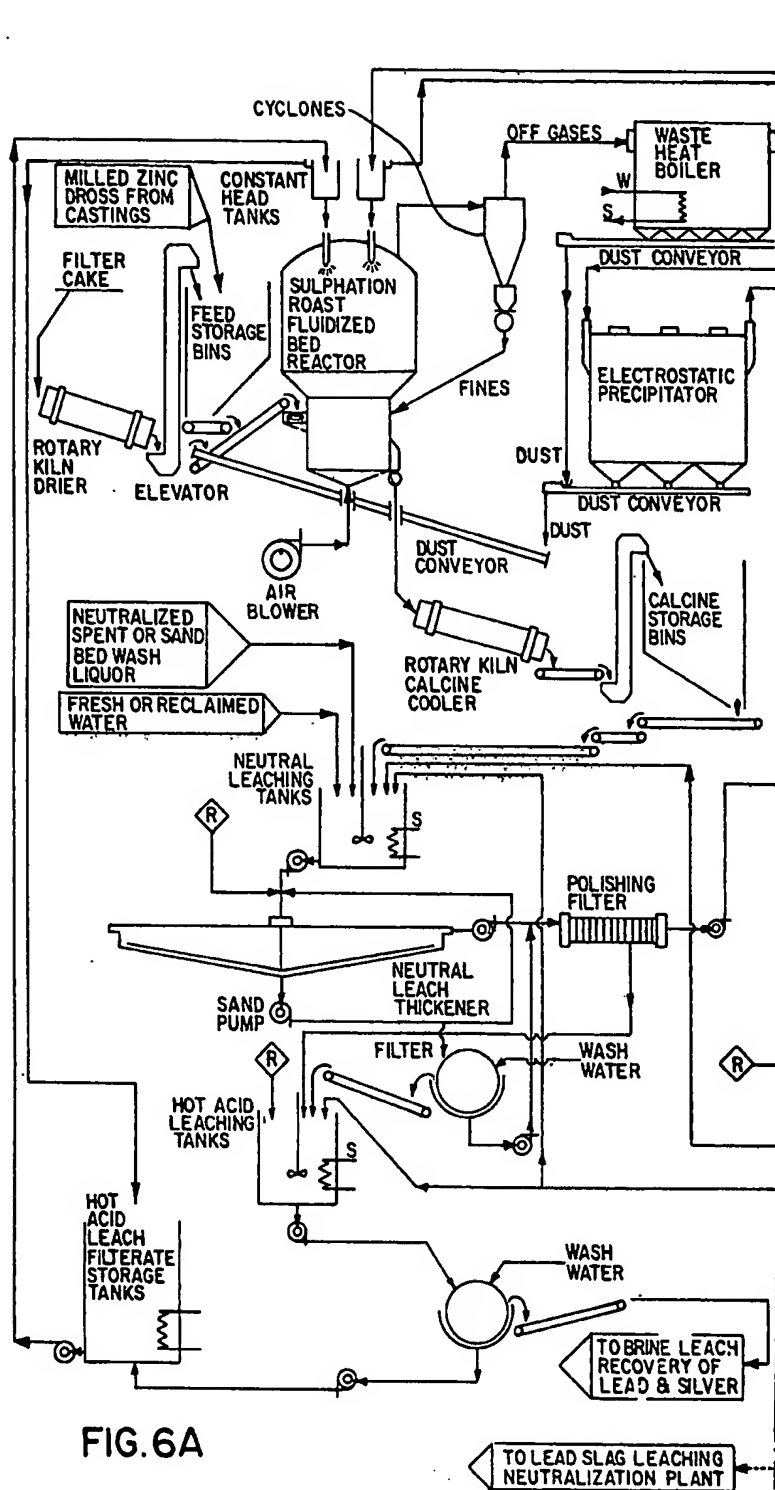
A = 1 % O_2 + 1 % SO_2 + 98 % N_2

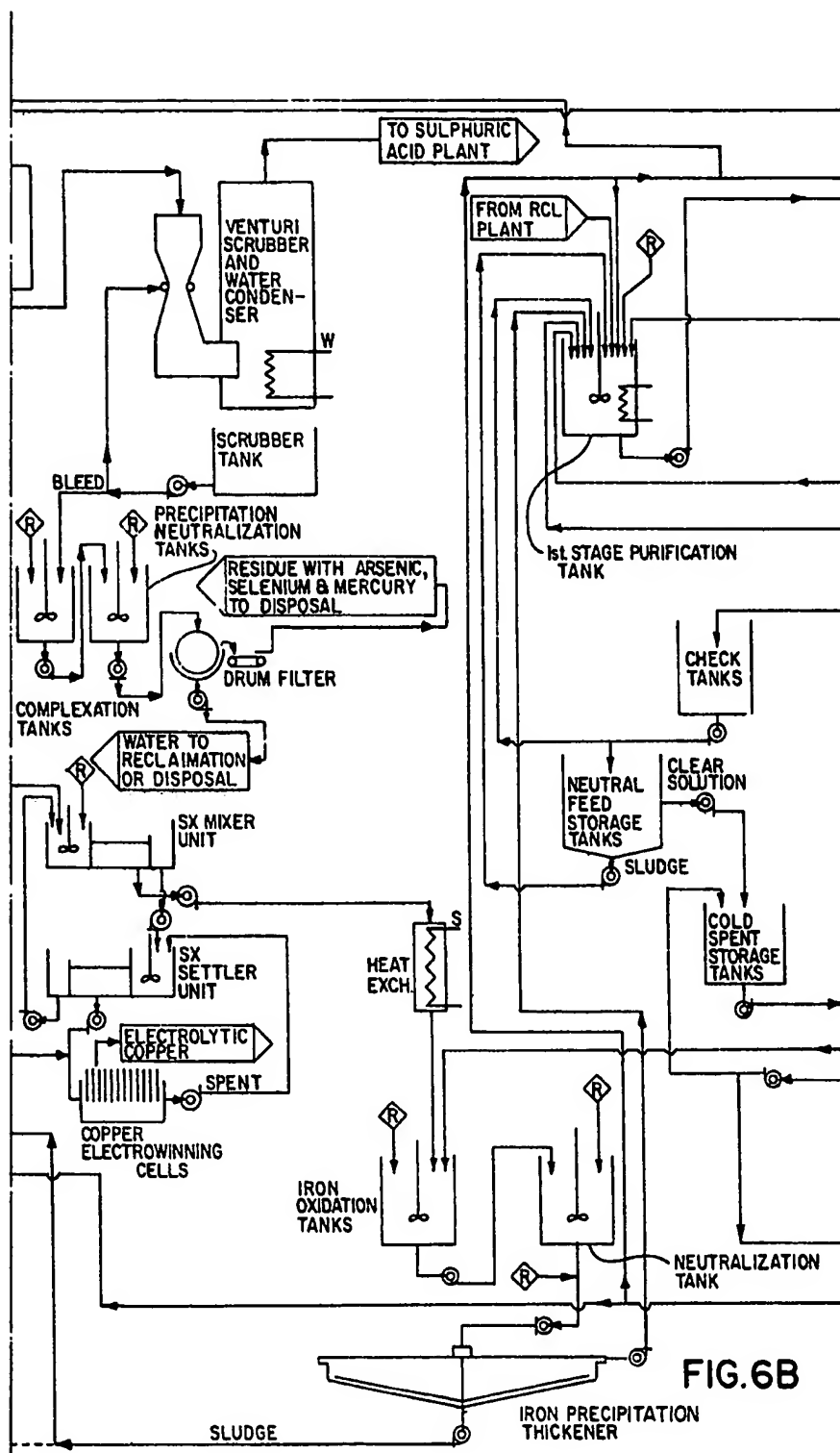
B = 10% O_2 + 1 % SO_2 + 88 % N_2

C = 10 % O_2 + 10 % SO_2 + 80 % N_2

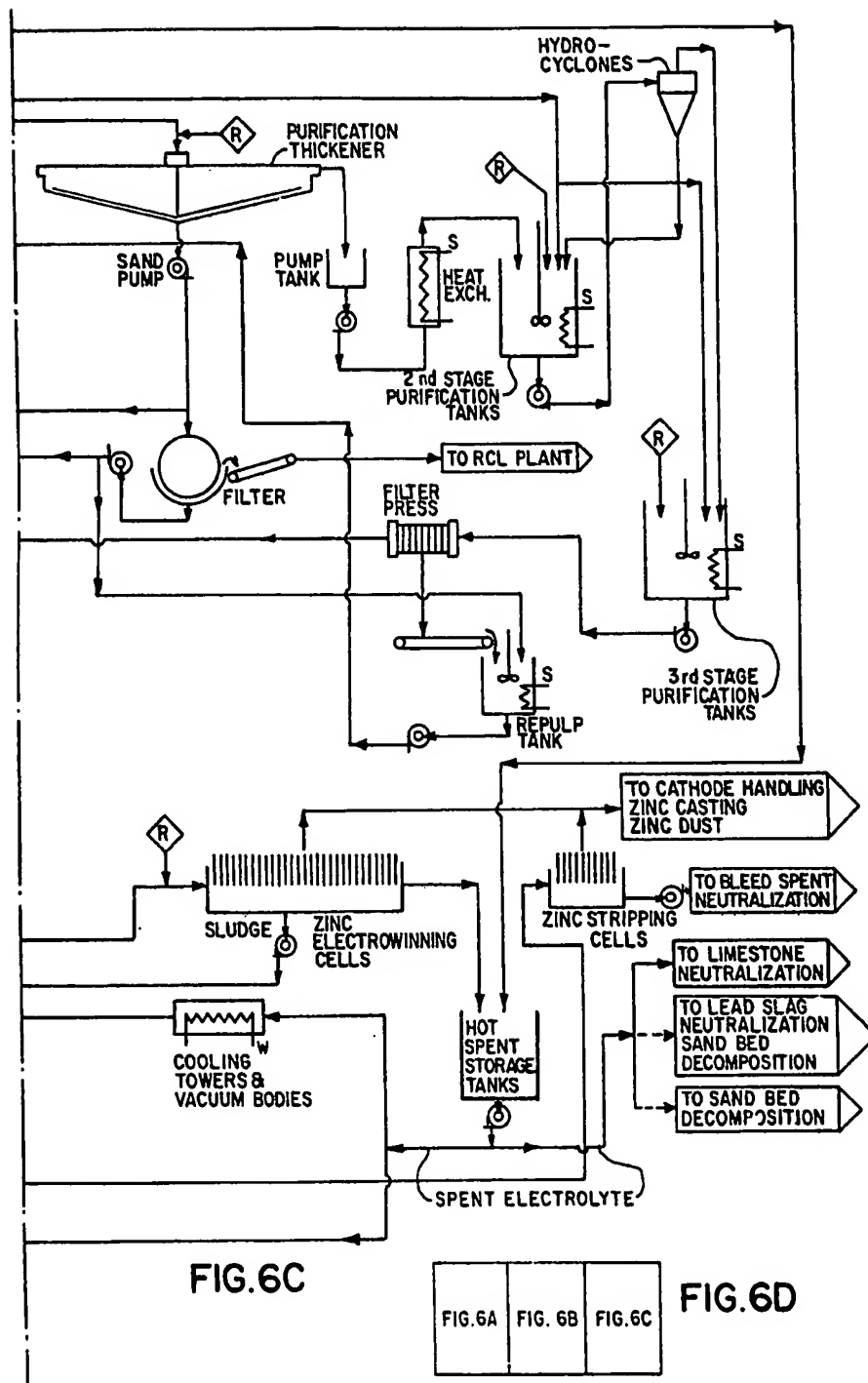
D = 1 % O_2 + 10 % SO_2 + 88% N_2

FIG. 5





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OFF GASES

WASTE HEAT BOILER

MILLED ZINC DROSS FROM CASTINGS

TO SULPHURIC ACID PLANT

DEAD ROAST FLUIDIZED BED REACTOR

DRY ZINC CONCENTRATE STORAGE BINS

FILTER CAKE OF ZINC CONCENTRATE FROM MILL

CALCINES

AIR BLOWER

VENTURI SCRUBBER AND WATER CONDENSER

SCRUBBER TANKS

COMPLEXATION TANK

PRECIPITATION NEUTRALIZATION TANK

DRUM FILTER

WATER TO DISPOSAL OR RECLAMATION

RESIDUE WITH ARSENIC, SELENIUM AND MERCURY TO DISPOSAL

1st. STAGE PURIFICATION TANKS

NEUTRAL FEED STORAGE TANKS

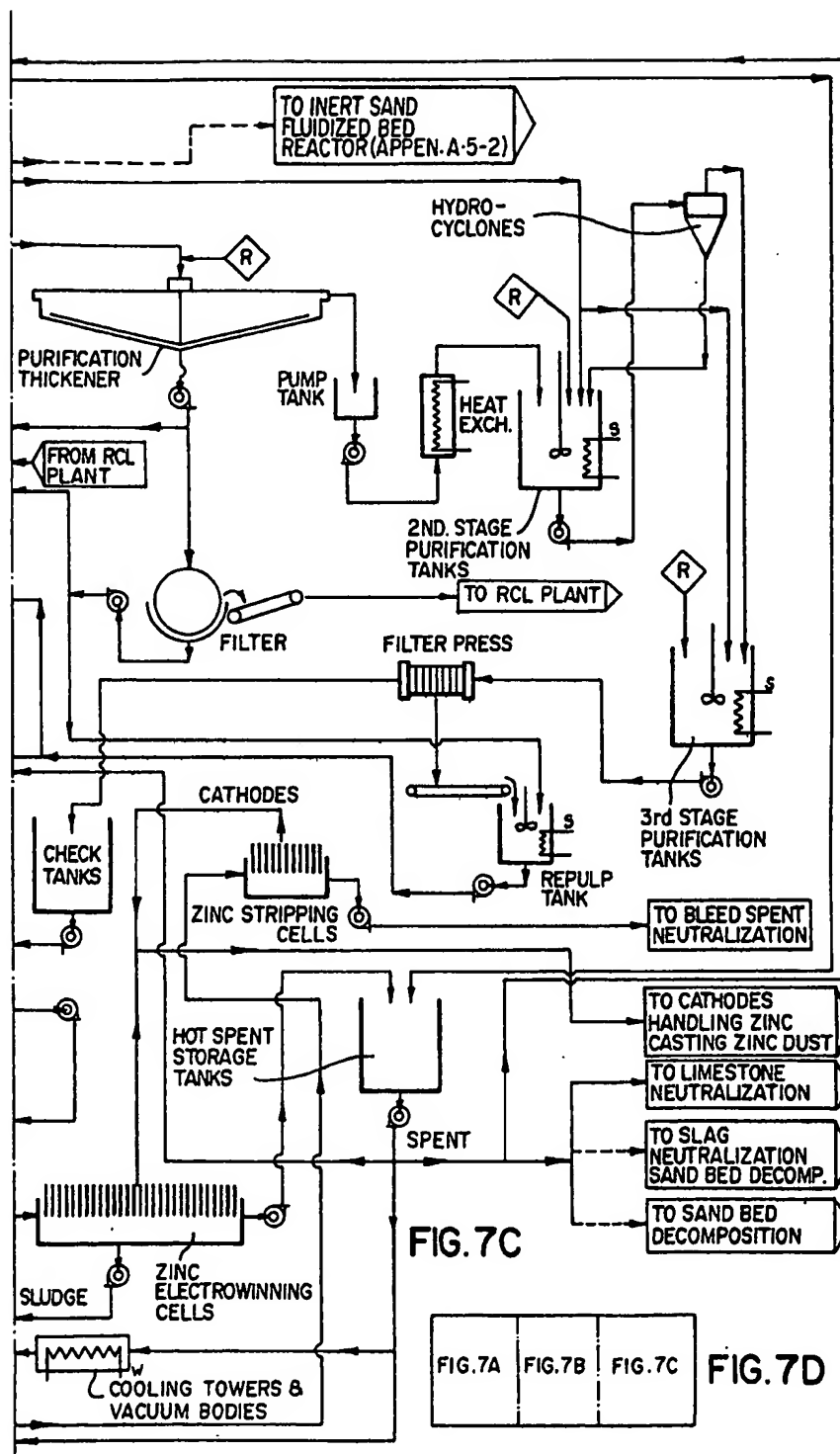
CLEAR SOLUTION

SLUDGE

COLD SPENT STORAGE TANKS

SPENT

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SPECIFICATION

Recovery of Non-Ferrous Metals by Thermal Treatment

This invention relates to a method to recover non-ferrous metals such as zinc or copper from their concentrates, ores or any other metal containing materials into a solution containing these non-ferrous metals as sulphates and a minimal amount of dissolved iron. The resultant solution is suited without or with minimum pre-purification treatment for conventional electrowinning processes to recover such non-ferrous metals with less difficulties than the previous methods involving complex iron-removal processing. More particularly, this invention relates to a method for recovering non-ferrous metals such as zinc, from a strong sulphuric acid solution which contains said metals and iron as sulphates with less difficulties than the previous methods involving complex iron-removal processing.

During the roasting of zinc mill products either by sulphation or dead roasting, a quantity of zinc, generally representing up to 40% by weight of the total zinc in a feed, forms as the refractory compound ferrite (ZnFe_2O_4) which remains insoluble in the standard dilute acid leach ("neutral leach") used in the zinc industry. Although zinc ferrite can be leached in strong sulphuric acid solutions, the resulting iron also brought into solution by said strong acid treatment must then be removed in a conventional zinc plant practice prior to zinc electrolysis.

Several technologies have evolved for the removal of iron from solutions resulting from the strong acid leaching of ferrite residues. The more common of these in commercial usage include the jarosite process (Australian Pat. 401,774, Mar. 31, 1965; U.S. Pat. 3,493,365, Feb. 3, 1970; Spanish Patent 304,601, Oct. 12, 1964; U.S. Pat. 3,434,798, Mar. 25, 1969; Norwegian Pat. 108,047, April 30, 1965; U.S. Pat. 3,434,947, March 25, 1969); the goethite process (Belgian Pat. 724,214, Nov. 20, 1968; U.S. Pat. 3,652,264, March 28, 1971); and the hematite process (Australian Pat. 247,274, Dec. 5, 1960; U.S. Pat. 3,143,486, Aug. 4, 1964; Australian Pat. 255,428, Jan. 11, 1961; U.S. Pat. 3,193,382, July 6, 1965).

The jarosite process employs the addition of sodium, potassium or ammonia compounds to effect the precipitation of crystalline iron jarosites, which can be settled, filtered, washed and finally discarded more readily than can ferric hydroxide. The goethite process is somewhat similar to the jarosite process but is more energy-consuming and is somewhat dependent on the availability of low-cost steam. In the hematite process, iron is precipitated from solution, at 200°C under pressure, as Fe_2O_3 .

Although the jarosite, goethite and hematite processes have been effective in increasing zinc recoveries in the electrolytic process from the

range 85—93% by weight to 96—98% by weight, the technologies are complex and energy-intensive. In the case of the more commonly employed jarosite process, the recovery of zinc from ferrite by a strong acid leach of the dilute acid leach residue rarely exceeds 70%. This represents a loss of 2—4% of the total zinc in the roaster feed. Also, the disposal of the voluminous jarosite precipitates is now being recognized as an environmental problem.

Apart from what is now conventional practice, that is, chemical dissolution of ferrite and subsequent iron handling, attempts have also been made to resulphate ferrite residues in a fluidized bed reactor (Steinveit, G. 1970, AIME World Symposium on Mining and Metallurgy of lead and zinc, vol. 11, p. 229; Alain S. Gill and Ralph W. Pickering, Can. Pat. 566,126, Nov. 18, 1958; Tanner, H. and Nyholm, E., Can. Pat. 851,656, Sept. 15, 1970; Moriyama, E., Ito, T., and Yamamoto, Y., Jap. Pat. Appl. Pub. No. 20881/68, Sept. 9, 1968, Jap. Pat. 537551). The reaction rates for the resulphation of ferrite however are sluggish. This, plus other operational difficulties, results in a comparatively (with the jarosite process) uneconomic technique for decomposing ferrite.

Many other processes for handling zinc ferrites, such as the E. Z. process (Australian Pat. 424,095, May 15, 1970; U.S. Pat. 3,781,405, Dec. 25, 1973), and chlorination roasting (A. Roeder, H. Junghanns and H. Kudelka, J. of Metals, 12, pp. 31—37, 1969), have been proposed but are presently not employed commercially to the knowledge of the inventors.

The primary object of this invention is to provide a method for recovering zinc preferably from relatively low-grade zinc-bearing concentrates with less difficulty than the previous methods involving complex iron-removal processing.

Another object of this invention is to provide such a zinc-recovering method as above, wherein said method can be combined with a conventional dead roasting method to the overall benefit of the zinc recovery process.

A further object of this invention is to provide a method for recovering non-ferrous metals soluble in sulphuric acid from a concentrated sulphuric acid solution which contains said metals and iron as sulphates, with less difficulties than previous methods involving complex iron-removal processing prior to electrolysis or other metal recovery processes.

In one aspect of this invention there is provided a method for recovering at least one non-ferrous metal soluble in sulphuric acid from a strong sulphuric acid solution containing said metal and iron as sulphates, said method comprising the following consecutive steps:

subjecting said solution in a sub-divided form to thermal decomposition in a fluidized bed reactor at a temperature of from 600 to 750°C with 20—150% excess air for an average retention time of 1—12 hours to obtain calcine

containing ferric oxide and the sulphate of said non-ferrous metal;

leaching said non-ferrous metal sulphate out from said calcine with water or dilute sulphuric acid solutions;

separating said leach solution containing said non-ferrous metal sulphate from the residue; and recovering said non-ferrous metal from said leach solution, via electrolysis or any other method.

In a further aspect of this invention there is provided a method for recovering at least one non-ferrous metal soluble in sulphuric acid from a solid material containing said non-ferrous metal and iron, comprising:

(a) roasting said material in a subdivided form in a fluidized bed reactor at a temperature from 600 to 750°C, with 20—150% excess air for an average retention time of 1—12 hours resulting in an atmosphere comprising SO₂, SO₃, water vapor and remaining O₂ and N₂ from the air, to obtain a calcine containing ferrite and sulphates, oxysulphates and oxides of said non-ferrous metal, plus hematite;

(b) leaching said calcine with water or dilute sulphuric acid solution in such a manner that the sulphates, oxysulphates, and oxides of said non-ferrous metals are leached out in part from the calcine into the water or dilute sulphuric acid solution;

(c) subjecting the leach pulp resulted from step (b) to a liquid-solid separation step to yield a leach solution suitable for purification metal recovery steps for said non-ferrous metal;

(d) leaching the solid residue resulted from step (c) with strong sulphuric acid solution in such a manner that the ferrite and unreacted sulphides of said non-ferrous metal are converted to the sulphates of iron and said non-ferrous metal;

(e) subjecting the pulp resulted from step (d) to a liquid-solid separation step to obtain a leach solution containing said sulphates of iron and said non-ferrous metal; and

(f) recycling a said solution obtained in step (e) into said fluidized bed reactor in a subdivided form to convert the sulphates of iron to ferric oxide, SO₂ and SO₃ and sulphuric acid to SO₂, SO₃ and gaseous H₂O.

In a still further aspect of this invention there is provided a method set forth in the immediately preceding paragraph, in which calcine from a dead roaster and calcine from the sulphation fluidized bed reactor are leached with dilute sulphuric acid solution(s) and the strong acid leach solution is recycled to the sulphation roaster.

The present invention will be more fully appreciated by the following detailed description of embodiments of the invention, referring to the accompanying drawings, in which:

Fig. 1 is a schematic flow sheet illustrating an embodiment of the sulphation roasting process applied to a low grade zinc concentrate according to this invention;

Fig. 2 is a schematic flow sheet illustrating an

embodiment of the integrated sulphation roasting and dead roasting processes applied to a low grade zinc concentrate and a high grade zinc concentrate, respectively, according to this invention;

Fig. 3 is a schematic flow sheet illustrating an embodiment of the sulphation roasting process according to the present invention, applied to treat ferrite residues from a dead roasting of high grade zinc concentrates operation alone;

Fig. 4 is a schematic flow sheet illustrating an embodiment of the sulphation roasting process according to the present invention, applied for the recovery of metals from a solution containing sulphates of said metals and iron by thermal decomposition of the iron sulphates to ferric oxide;

Fig. 5 is a phase stability diagram;

Fig. 6 is a schematic plant layout related to Example 1; and

Fig. 7 is a schematic plant layout related to Example 2.

In the present invention, the difficulties and complexities of treating and separating the iron in solution after the ferrite or other zinc residues are leached are substantially eliminated by thermal decomposition of the strong sulphuric acid leach solution at 600—750°C in a fluidized bed reactor. Use is made of the excess heat produced from the oxidation and sulphation reactions of the feed in the bed. The zinc and other metals such as copper remain as solid sulphates and oxysulphates in the roaster calcines and can be recovered totally or in part with a water or dilute sulphuric acid leach. All iron sulphates in the strong acid leach solution are decomposed in the roaster to hematite and SO₂ and SO₃, and the sulphuric acid to H₂O, SO₂ and SO₃. The hematite remains inert in the subsequent water or dilute sulphuric acid leach.

The present invention overcomes one of the major limiting factors in current electrolytic zinc plant practice, i.e., the handling of relatively high-iron-containing zinc concentrates.

In conventional dead roasting processes a bulk of iron in a zinc concentrate serves to tie up zinc as ferrite (ZnFe₂O₄) in calcine. As a result, high-iron zinc concentrates are generally considered to be unsuitable feed to most existing electrolytic zinc plants. However, in sulphation roasting only a little fraction of the iron ends up as ferrites, the remainder forms hematite (Fe₂O₃). A low grade zinc concentrate, for example, of 30% by weight of Zn and 22% by weight of Fe, in a sulphation roast, would result in less than 15% by weight of the total zinc as ferrite, whereas a conventional dead roast of the same concentrate might tie up approximately 40% of the zinc as ferrite. Hence the combination of a sulphation roast plus the recycle of the strong sulphuric acid leach filtrate of the ferrite residue back to the sulphation roaster can be used to treat low grade zinc concentrates which are not amenable to current electrolytic zinc plant technology.

This invention then is of special interest to

producers of zinc concentrates from ores where physical constraints such as grinding liberation result either in low grade concentrates or unacceptably high metal losses to tailings. Such losses generally result in a compromise in producing concentrates of a grade acceptable to current electrolytic zinc plants.

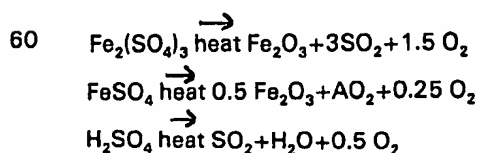
Any metal-rich sulphate solution derived either from leaching of roaster calcines or leach residues or other metallurgical slags, but most particularly those leach solutions high in iron, such as would be derived from strong sulphuric acid leaching of ferrite residues which would require a post-leach iron removal stage, are suitable feed solutions for decomposition in a fluidized bed roaster under sulphating conditions. Also suitable are certain bleed and waste streams from metallurgical plants, which carry metals such as zinc and copper as well as iron, e.g., pickling liquors.

Referring now to Figure 1, the leaching of refractory zinc compounds such as zinc ferrite residue resulting from dilute sulphuric acid leaching is carried out continuously at over 40°C for over one-half hour at a pH less than 2.0, but preferably at 95°C, with 40 gpl free H₂SO₄ for 2 hours. Under these preferable conditions over 95% of the zinc from zinc ferrite and greater than 85% of the zinc from remnant sphalerite can be leached. To achieve highest extraction of zinc from sphalerite it is desirable that the zinc ferrite/sphalerite ratio not be less than 3/1. The ferric iron from dissolved ferrite is the principal leaching agent in dissolving sphalerite.

The pulp, after the strong sulphuric acid leaching step, is filtered in a filter press or any other suitable equipment, and the residue, predominantly hematite, is washed with hot water or hot dilute sulphuric acid, preferably over 90°C with a volume preferably no larger than about two times the volume of the entrapped water in the residue.

The solution coming from the filtering step, is then thermally decomposed by spraying with compressed air, or any other suitable method, into a suitable reactor such as a fluidized bed that operates at over 600°C, with over 20% excess air over the stoichiometric and with an average retention time for the solid over 1 hour, but preferably at 685°C with 85% excess air and for 5.5 hours average retention time. The solution contains up to 225 gpl Fe as Fe₂(SO₄)₃ and FeSO₄, 200 gpl Zn as ZnSO₄, 100 gpl Cu as CuSO₄, 300 gpl H₂SO₄, and some impurities such as As.

At the temperature of the reactor, water from the solution vaporizes readily, followed by the thermal decomposition of iron sulphates to Fe₂O₃ and SO₂ and SO₃ and sulphuric acid to SO₂ and SO₃ and H₂O. These endothermic reactions are as follows:



ZnSO₄ and CuSO₄, which are thermodynamically stable at 685°C remain as such in the small porous pellets formed during the spraying of the solution, and act as binder for the hematite formed from the decomposition of the iron sulphates. The pellets, which become fully mixed with the calcine inside the fluidized bed, increase the size distribution in the total bed material and hence also considerably improve the fluidization properties of the calcine. The thermodynamic stability of these three compounds, ZnSO₄, CuSO₄ and Fe₂O₃ is illustrated from the combined phase diagrams for the systems Zn—S—O, Cu—S—O and Fe—S—O at 685°C, shown in Fig. 5. Under all roasting conditions for SO₂ concentrations of 3 to 15%, ZnSO₄ and CuSO₄ are the only stable sulphates while iron sulphates decompose to Fe₂O₃. For SO₂ concentrations less than about 2%, some copper and zinc oxysulphates can be present, which also are soluble in dilute sulphuric acid.

Figure 5 illustrates the normal range for SO₂ and O₂ composition in sulphation roasting. The shadowed area ABCD represents conditions where at C the gases in the roaster contains 10% SO₂ and 10% O₂. The stable compounds formed under these conditions are ZnSO₄ and CuSO₄, which are soluble in water or dilute acid and Fe₂O₃, which is insoluble in water or weak acid.

Any increase in SO₂ concentration from point C will favour the formation of FeSO₄ which is a water or dilute acid soluble compound and hence would result in increased quantities of iron in leach solutions which would be an undesirable feature in zinc plant practice.

Diagonally opposite from C at point A, where the gas is composed of 1% SO₂ and 1% O₂, ZnSO₄, Fe₂O₃ and CuO.CuSO₄ are the stable phases. Any further downward trend from A i.e. lower SO₂ concentration, will favour the formation of ZnO.2ZnSO₄. This should also be avoided as ZnO.2ZnSO₄ can react with Fe₂O₃ during roasting to form ZnFe₂O₄ (ferrite) which is soluble only in strong acid solutions.

At point B, (1% SO₂, 10% O₂) both CuSO₄ and CuO.CuSO₄ are stable phases with ZnSO₄ and Fe₂O₃. At point D (10% SO₂, 1% O₂) the compounds formed are the same as at point C.

A decrease in roasting temperature will displace all phase boundaries in Figure 5 towards the lower left. This will effectively increase the stability fields of all sulphates including iron sulphates, FeSO₄ and Fe₂(SO₄)₃. As the iron level in leach solutions should be kept to a minimum, it is important that the roasting temperature not be appreciably below 685°C. Conversely, increasing roasting temperatures above 685°C will favour the formation of ZnO.2ZnSO₄ and undesirable ferrite. The latter being formed either directly or by reaction of ZnO.2ZnSO₄ with Fe₂O₃.

Volatile impurities such as As, Sn, Sb, Cl, etc., achieve an equilibrium balance in the calcine and hence virtually all freshly introduced volatiles exit with the off gases.

The discharge from the roaster overflow, which

represents 100% of the reactor discharge since the elutriated solids in sulphation roasting are continuously recirculated back to the reactor, is then cooled in a rotary cooler or other suitable device. Leaching is carried out in water or dilute sulphuric acid but generally with dilute sulphuric acid under conditions over 15°C, pH 7.0 or lower and over one-half hour retention time, but preferably similar to conditions employed in 'neutral leach' circuits in conventional electrolytic zinc plants.

When a dilute sulphuric acid leaching is used in this step, all ZnSO_4 , CuSO_4 , and most of the zinc and copper oxysulphates are solubilized. The pulp is settled or filtered. The filtrate generally contains up to 180 gpl Zn, 50 gpl Cu, with less than 1 gpl Fe. The residue consists mostly of hematite and also of small amounts of zinc precipitated from the oxysulphate plus all of the ferrite and remnant sphalerite produced from the fresh feed to the roaster. This residue is then leached with strong sulphuric acid as described above.

The process therefore incorporates a closed loop where the zinc present as ferrite and sphalerite in the residue from the dilute sulphuric acid leach is solubilized in hot strong sulphuric acid and the resultant metal/sulphate solution is decomposed in the fluid bed reactor. In this manner, virtually all of the zinc and copper are effectively recovered through the 'neutral leach' circuit to purification with solutions containing less than 1 gpl iron. Thus the need for complex iron precipitation and disposal procedures such as those required in the jarosite process is substantially simplified.

The level of copper in the roaster feed material and its concentration in the dilute sulphuric acid leach filtrate determine a suitable procedure for copper recovery. If the copper content is sufficiently high, then solvent extraction, with or without electrowinning may be incorporated in the purification circuit; otherwise the copper would be cemented as in conventional zinc plant practice.

An added advantage of this process is in the increased strength of the SO_2 and SO_3 in the dry roaster off gases. The concentration of these gases is increased by as much as 30% with the decomposition of the strong sulphuric acid leach solution recycle in the roaster. This increased gas strength is desirable for the manufacture of sulphuric acid from roaster off gas.

As illustrated in Figure 2, the sulphation roasting process of this invention can be used in conjunction with conventional dead roasting of standard zinc concentrates to eliminate the jarosite or other iron precipitation stages in conventional electrolytic zinc plants. The sulphation reactor operates at a temperature between 600 and 750°C, preferably at 685°C, and the dead roast at a temperature between 880°C and 1000°C, preferably at 930°C. Calcines discharging from both reactors are cooled as in conventional zinc plant practice and described above with respect to the embodiment

illustrated in Figure 1. The residue, after dilute sulphuric acid leaching and subsequent filtering, contains all the ferrite and remnant sphalerite produced in both sulphation and dead roasting operations, and is subjected to a strong sulphuric acid leaching in the manner described above to dissolve the ferrite and most of the sphalerite. The pulp is filtered as described above and the filtrate is then recirculated back into the sulphation reactor to decompose the iron sulphates and sulphuric acid and recover the zinc and copper in the same manner as described above. The two stage leaching operation can be carried out on a combined calcine from both the sulphation roaster and dead roaster, as illustrated in Figure 2, or in separate leach trains or in semi separate circuits with the final strong acid leach solutions being recycled to the sulphation roaster.

The strong sulphuric acid leach filtrate must be decomposed in the sulphation reactor, where conditions preclude the formation of much ferrite from the solution. At dead roast temperatures most if not all of the iron in solution would combine again with zinc to form zinc ferrite.

As the level of ferrite (and sphalerite) dissolution in the strong sulphuric acid leach is much higher in the present sulphation roasting process than in conventional zinc plant practice, i.e., over 95% dissolution versus 70%, overall zinc extraction from the dead roast calcine using the present sulphation roasting process, will be improved. Together with the high extraction of zinc and copper, the iron precipitation problem, which is characteristic of current electrolytic zinc plant practice is reduced, as substantially all iron is converted to insoluble, easily filterable, Fe_2O_3 (hematite), in the calcine. This effectively eliminates the requirement for a jarosite or other iron precipitation process now required in conventional electrolytic zinc plants.

The thermal balance in the integrated sulphation roasting/dead roasting can be adjusted in such a form that all of the strong sulphuric acid leach solution recycle resulting from the dissolution of both ferrite residues from the sulphation and dead roasting neutral leach can be decomposed in the sulphation roaster keeping the thermal balance with no external fuel addition. For example, when a concentrate of 30.6% Zn by weight is used in the sulphation roasting and a 55% Zn by weight concentrate as feed for the dead roaster, the feed ratio to the sulphation roaster/dead roaster should be equal or greater than 1.45/1. In this case, the sulphation roaster is thermally autogeneous and no external fuel is required. If this ratio is less than 1.45, additional fuel would be required for the sulphation roaster in a form of natural gas, oil or other fuel to maintain the thermal balance.

A feed ratio of 1.45 represents about 45% of the zinc produced from the sulphation roaster using said feed of 30.6% Zn by weight, and 55% of zinc produced from the dead roaster using said feed of 55% zinc by weight. This ratio nevertheless is dependent on the grade and

mineralogy of the products used and the ratio 1.45 applies only for the 30.6 and 55% Zn case where the dominant minerals in the concentrates are sphalerite and pyrite. Also this ratio does not take into consideration heat available in the roaster freeboard for decomposing the strong acid leach solutions, in which case a substantial decrease in the ratio may be achieved. Also, the ratio calculation is based on a combined sulphation roast-dead roast calcine leach. If separate leach trains are used the ratio could be decreased further.

The sulphation roasting process according to this invention can be used to treat ferrite residues from a dead roasting operation alone, as illustrated in Figure 3. In this case, the ferrite residues are leached in the same manner as described above.

The pulp following the strong acid leach contains little solids and can be recycled, in total, as a spray to an inert fluidized sand bed at a temperature between 600 and 750°C, preferably 685°C. The hot gases from the dead roasting operation, after cyclone cleaning, can be used to fluidize a bed of sand such as fine quartz or any other inert solid material of a size range approximating from No. 140 to No. 10 in the U.S. standard sieve series (105 μm to 2000 μm). The off gases from the dead roaster, at about 900°C, vaporize and decompose the strong sulphuric acid leach filtrate sprayed into the inert fluidized sand bed reactor in the same manner as explained above. In this way the zinc from the solution is recovered as zinc sulphate, while the iron decomposes to inert hematite. To achieve proper decomposition, the bed is maintained at 685°C by balancing the amount of gas passed through the bed with the amount of solution decomposed. The bed overflow, consisting of sand and the small pellets of zinc sulphate and hematite, is subjected to a water or dilute acid leach, for example 25 gpl H_2SO_4 , to recover the zinc. The sand is then classified and recirculated back to the reactor.

This alternative for handling ferrite residues from zinc plants has several advantages over present conventional techniques such as the jarosite process. No additional external energy over that extracted from the dead roaster off gas is required, iron forms as relatively easily filterable hematite and the zinc solution can be easily integrated with the main zinc electrolytic circuit. In addition, the quantity and concentration of SO_2 and SO_3 dry off gas from the roaster is increased by the decomposition of the iron sulphates and sulphuric acid in the sand bed. The sand bed itself also acts as a dust collector, simplifying the cleaning system for the bed off gases. The iron (hematite) residue as a waste product is less voluminous than normal jarosite residues and in general would reduce environmental problems.

The application of the sulphation roasting process according to this invention can be further extended to recover any metals which are soluble in sulphuric acid, as illustrated in Figure 4. The

metal-bearing material is leached with strong sulphuric acid solution in the manner described above. The pulp, if it contains insolubles, is filtered and the filtrate decomposed in a fluidized bed at a temperature between 600 and 750°C, preferably 685°C. The bed can be similar to the inert fluidized sand bed described above with respect to the embodiment in Figure 3, using hot gases from other operations or by heating the reactor with a suitable fuel such as natural gas, coal, oil, etc. The bed overflow, containing the soluble metal pellets with the hematite and the inert sand is subjected to a water or dilute acid leach and the sand is then separated, filtered, and the solution is further treated to recover the metal values. For example, this can be applied to the leaching of slags from a lead smelter to recover zinc as an alternative to the zinc fuming process.

Example No. 1:

Application to a sulphation Roast-Leach-Electrowinning Process for Relatively Low Grade Zinc Concentrates

A zinc middlings products from a zinc-lead-copper flotation mill assaying 30% Zn, 3.6% Pb, 0.6% Cu, and 22.38% Fe, with principal mineral components being sphalerite, galena, chalcopryrite and pyrite, was roasted in a continuous semi-pilot fluid-bed reactor at a rate of 120 kg per day under conditions where zinc, lead and copper are selectively sulphated and iron forms the oxide hematite. Sulphation roasting was carried out at 685°C with 85% excess air for an average retention time of 6.0 hours. Calcines from the overflow were leached with dilute sulphuric acid solution (containing 50 gpl Zn) at 50°C, 1.5 hours retention time at constant pH 4. The pulp from this dilute sulphuric acid leach was filtered and the solid residue leached in concentrated acid of constant 40 gpl free H_2SO_4 for a 2-hour retention time at 95°C. The strong sulphuric acid leach pulp was filtered, washed with hot water and the filtrate sprayed inside the same fluidized bed reactor which produced the calcine. The results are as follows:

		(by weight)
110	Initial Zn extraction in dilute sulphuric acid from calcine	=84.6%
	Initial Cu extraction in dilute sulphuric acid from calcine	=80.8%
115	Secondary Zn extraction in strong sulphuric acid from residue	=90.3%
	Secondary Cu extraction in strong sulphuric acid from residue	=89.5%
120	Overall extraction in dilute acid from calcine including decomposed strong acid leach filtrate	
125	Zn	=98.5%
	Cu	=98.0%
	Fe	=0.9%

Final dilute acid leach filtrate contains:

Zn	=150.0 gpl
Cu	=1.8 gpl
5 Fe	=0.7 gpl

By comparison, concentrates with levels of zinc and iron indicated in this example (30% Zn, 22.38% Fe) would not be generally acceptable to conventional dead roast-electrolytic zinc plants.

10 An unacceptable amount of zinc would end up as ferrite in the dead roast calcine and this would necessitate the handling of much more iron via precipitation techniques such as are used in the Jarosite process. The cost per unit of recoverable zinc would be much higher than for higher grade concentrates and the overall zinc recoveries would be approximately 10% less than would be achieved by the sulphation roast process outlined in Example 1.

20 The basic flow sheet for this example is illustrated in principle in Figure 1. Figure 6 is a schematic plant layout for a proposed sulphation roast-leach-electrowinning plant to treat this type of product.

25 Example No. 2:

Application to an Integrated Sulphation Roast-Dead Roast-Leach-Electrowinning Plant

30 A zinc middlings product from a zinc-lead-copper flotation mill assaying 32.03% Zn, 0.55% Cu, 3.50% Pb and 22.53% Fe, with principal mineral components being sphalerite, galena, chalcopryrite and pyrite, was roasted in a continuous semi-pilot fluidized bed reactor at a rate of 120 kg per day under conditions where zinc, copper and lead are selectively sulphated and iron forms the oxide hematite. Sulphation roasting was carried out at 685°C with 80% excess air for an average retention time of 6.0 hours.

40 Calcines from the sulphation roasting operation were combined in an equivalent weight ratio of the middlings and concentrate feeds of 1.43 to 1 with dead roasted calcines produced from a zinc concentrate containing 54.9% Zn, 45 0.57% Cu, 0.60% Pb and 10.37% Fe, and leached together with dilute sulphuric acid solution (containing 50 gpl Zn) at 50°C for 1.5 hours retention time at constant pH 4. The pulp from this dilute sulphuric acid leach was filtered and the solid residue submitted to a strong acid leach at constant 40 gpl free H₂SO₄ for a two hours retention time at 95°C. The resulting pulp was then filtered and washed with hot water and the filtrate and wash solution obtained were 50 continuously sprayed inside the sulphation fluidized bed reactor. Reactor operates without external thermal energy. Resulting calcine was leached with a dilute sulphuric acid solution (50 gpl Zn) for 1.5 hours at pH 4 at 50°C. The results are as follows:

Initial Zn extraction in dilute sulphuric acid from combined calcines	=86.5%
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65 Initial Cu extraction in dilute sulphuric acid from combined calcines =52.9%

Secondary Zn extraction in strong sulphuric acid from common residue =87.6%

70 Secondary Cu extraction in strong sulphuric acid from common residue =96.3%

75 Overall extraction in dilute acid from both calcines, including the decomposed strong acid leach filtrate

Zn	=98.3%
Cu	=98.3%
Fe	=1.0%

80 Final dilute acid leach filtrate contains

Zn	=149.50 gpl
Cu	=1.41 gpl
Fe	=0.60 gpl

85 When potassium permanganate was added to the dilute acid leach at 150% of stoichiometric for ferrous oxidation to ferric with simultaneous air sparging of the leach solution, the iron level in dilute acid leach liquor dropped to less than 0.02 gpl.

90 By comparison, with conventional dead roast zinc plant practice, the overall zinc recoveries via the integrated sulphation roast-dead roast are improved by approximately 1.5%. Whereas ferrite dissolution by strong acid leaching of ferrite residues in conventional zinc plant practice seldom exceeds 70%, dissolution of ferrite from the integrated sulphation roast-dead roast plant approaches 90%. Also important is the 100 simplification of the plant through the elimination of the iron precipitation stage such as the Jarosite process.

The basic flow sheet for this example is illustrated in principle in Figure 2. Figure 7 is a schematic plant layout for a proposed integrated sulphation roast-dead roast plant.

Example No. 3:

Application to a Conventional Dead Roast Zinc Plant to Replace the Iron Precipitation Stage as Exemplified by the Jarosite Process

110 A ferrite residue containing 36.4% Zn, 2.7% Cu acid and 53.7% Fe, obtained from the neutral leach of a dead roasted zinc concentrate, was submitted to strong sulphuric acid leaching at a constant level of 40 gpl H₂SO₄ for two hours at 95°C. The resulting pulp was filtered and washed with hot water and the filtrate obtained sprayed into a semi-pilot fluidized bed reactor at a flow rate of 94 1t/day. The bed in the fluidized bed reactor consisted of silica sand, having a size range between No. 140 to No. 60 (105 µm to 250 µm) in the U.S. Standard Sieve Series. The small pellets formed by decomposition of the solution sprayed and the sand bed were fluidized 125 with air. Heat was applied externally to maintain the temperature at 685°C.

The fluidized bed overflow discharged continuously into a quenching solution of pH 4 sulphuric acid to leach the zinc and copper from the pellets and sulphate-coated sand grains. The resulting pulp was filtered and washed to recover the dissolved zinc and copper from the insoluble sand, hematite and other impurities.

The results are as follows:

		(by weight)
10	% Zn extracted in strong sulphuric acid from residue	=85.1%
	% Cu extracted in strong sulphuric acid from residue	=97.8%
15	% Fe extracted in strong sulphuric acid from residue	=94.2%
	% Zn extracted from leaching of sand bed calcine	=99.9%
	% Cu extracted from leaching of sand bed calcine	=99.9%
20	% Fe extracted from leaching of sand bed calcine	=<0.1%
	Overall extraction of zinc from calcines in dilute acid leach, including the decomposed strong acid leach filtrate:	
25	% Zn extracted	=98.1%
	% Cu extracted	=99.8%
	% Fe extracted	=0.7%
30	Final dilute acid leach filtrate contains:	
	Zn	=150.0 gpl
	Cu	=1.04 gpl
	Fe	=0.54 gpl

When oxidants, such as KMnO_4 and air were added to the dilute acid leach, zinc and copper levels remain unchanged but iron dropped to less than 0.02 gpl.

By comparison with convention dead roast zinc plant practice, overall zinc recoveries are improved, using the sand bed decomposition of the strong acid filtrate, from 96.3% to 98.1%. A most important aspect of this invention is the elimination of the requirement for a complex iron precipitation process such as the Jarosite process from electrolytic zinc plant practice.

Example No. 4: Application to a Copper Leach Residue

A copper leach residue, from a roasted calcine, containing 9.2% Cu as cupric ferrite and minor amounts of covellite, 0.31% Co as cobalt ferrite $\text{CoO} \cdot \text{Fe}_2\text{O}_3$, and 48.18% Fe as Fe_2O_3 was leached at 95°C at a constant level of 50 gpl H_2SO_4 for 2.5 hours. The pulp was filtered and washed with hot water and the filtrate resulting was sprayed into a semi-pilot fluidized bed reactor at a rate of 67 t/day. The bed in the fluidized bed reactor consisted of silica sand having a size range between No. 140 to No. 60 ($105 \mu\text{m}$ to $250 \mu\text{m}$) in the U.S. Standard Sieve Series. The small pellets formed by decomposition of the solution sprayed and the sand bed were fluidized with air.

Heat was applied externally to maintain the temperature at 685°C.

The fluidized bed overflow discharged continuously into a quenching sulphuric acid solution of pH 4 to leach the copper and cobalt from the pellets and sulphate-coated sand grains. The resulting pulp was filtered and washed to recover the dissolved copper and cobalt for the insoluble sand, hematite and other impurities.

The results are as follows:

	% Cu extracted in strong sulphuric acid from residues	=92.3%
65	% Co extracted in strong sulphuric acid from residues	=88.9%
	% Fe extracted in strong sulphuric acid from residues	=26.0%
70	% Cu extracted from leaching of sand bed calcine	=+99.9%
	% Co extracted from leaching of sand bed calcine	=99.6%
	% Fe extracted from leaching of sand bed calcine	=<0.1%
	Overall extraction from sand bed calcines in dilute acid leach, including the decomposed strong acid leach filtrate:	
85	% Cu extracted	=92.3%
	% Co extracted	=88.8%
90	% Fe extracted	=<0.1%

When oxidants, such as KMnO_4 and air were added to the dilute acid leach, copper and cobalt levels remain the same but iron dropped to less than 0.03 gpl.

By comparison, when the strong acid leach filtrate is treated by iron cementation at 25°C for 12 hours, recovery of Cu as copper cement dropped to 78.2% while no cobalt was recovered.

The best mode of application for carrying out the invention would be on low grade zinc concentrates, (i.e. less than 45% zinc) which otherwise would not be readily acceptable to conventional electrolytic zinc plants. The sulphation roasting of such concentrates can be carried out either alone as in Example 1, or in combination with a conventional dead roast facility, as in Example 2.

The ferrite in the neutral leach residues are decomposed by strong sulphuric acid and the filtrate returned to the sulphation roaster as a coolant spray. Thermal decomposition of the filtrate in the roaster results in the contained iron being converted to the relatively insoluble Fe_2O_3 while zinc and copper remain as sulphates which are soluble in water and/or weak sulphuric acid.

Alternately the invention can be employed to replace present iron precipitation processes in conventional electrolytic zinc plants as shown by Example 3. The ferrite residues from conventional zinc plants are leached by strong sulphuric acid solution as in present practice. However, in place of the iron precipitation techniques, such as the Jarosite process, which are presently employed

the filtrate is decomposed in an inert fluidized sand bed under sulphating conditions. The iron sulphates are decomposed to the relatively insoluble stable Fe_2O_3 and as such the iron levels in the subsequent leach filtrate derived from the sand bed calcine are sufficiently low for the solution to be blended with the main zinc plant neutral leach solution entering the purification circuit without requirement for an iron precipitation stage such as the Jarosite process.

Claims

1. A method for recovering at least one non-ferrous metal soluble in sulphuric acid from a strong sulphuric acid solution containing said metal and iron as sulphates, said method comprising the following consecutive steps:
 subjecting said solution in a sub-divided form to thermal decomposition in a fluidized bed reactor at a temperature of from 600 to 750°C with 20—150% excess air for an average retention time of 1—12 hours to obtain calcine containing ferric oxide and the sulphate of said non-ferrous metal;
 leaching said non-ferrous metal sulphate out from said calcine with water or dilute sulphuric acid solutions;
 separating said leach solution containing said non-ferrous metal sulphate from the residue; and
 recovering said non-ferrous metal from said leach solution, via electrolysis or any other method.

2. The method as defined in Claim 1 wherein said sulphation roasting is carried out at 685°C, with 85% excess air for an average retention time of 5.5 hours.

3. The method as defined in Claim 1 wherein said leaching step is carried out at a temperature between 25 and 80°C at a pH between 0.3 and 7.0 and for an average retention time of 0.5 to 10 hours.

4. The method as defined in Claim 3 wherein said leaching step is carried out at 40—60°C, at pH 3.6—4.2 and for an average retention time of from 0.5 to 1.5 hours.

5. The method as defined in any one of Claims 1 to 4, wherein zinc and copper are recovered.

6. The method as defined in any one of Claims 1 to 4, wherein zinc is recovered.

7. A method for recovering at least one non-ferrous metal soluble in sulphuric acid from a solid material containing said non-ferrous metal and iron, comprising:
 (a) roasting said material in a subdivided form in a fluidized bed reactor at a temperature from 600 to 750°C with 20—150% excess air for an average retention time of 1—12 hours resulting in an atmosphere comprising SO_2 , SO_3 , water vapor and remaining O_2 and N_2 from the air, to obtain a calcine containing ferrite and sulphates, oxysulphates and oxides of said non-ferrous metal, plus hematite;
 (b) leaching said calcine with water or dilute sulphuric acid solution in such a manner that the sulphates, oxysulphates, and oxides of said non-

ferrous metals are leached out in part from the calcine into the water or dilute sulphuric acid solution;
 (c) subjecting the leach pulp resulting from step (b) to a liquid-solid separation step to yield a leach solution suitable for purification-metal recovery steps for said non-ferrous metal;
 (d) leaching the solid residue resulted from step (c) with strong sulphuric acid solution in such a manner that the ferrite and unreacted sulphides of said non-ferrous metal are converted to the sulphates of iron and said non-ferrous metal;
 (e) subjecting the pulp resulted from step (d) to a liquid-solid separation step to obtain a leach solution containing said sulphates of iron and said non-ferrous metal; and
 (f) recycling a said solution obtained in step (e) into said fluidized bed reactor in a subdivided form to convert the sulphates of iron to ferric oxide, SO_2 and SO_3 and sulphuric acid to SO_2 , SO_3 and gaseous H_2O .

8. The method as defined in Claim 7 wherein the step (a) is carried out at 685°C with 85% excess air for an average retention time of 5.5 hours.

9. The method as defined in Claim 7 wherein the step (b) is carried out at a temperature between 25 and 80°C, at a pH between 0.3 and 7.0, and for an average retention time of from 0.5 to 10 hours.

10. The method as defined in Claim 9 wherein the step (b) is carried out at 40—60°C, at pH 3.6—4.2, and for an average retention time of from 0.5 to 1.5 hours.

11. The method as defined in Claim 7 wherein the step (d) is carried out at a temperature between 40 and 100°C, for an average retention time between one-half and 10 hours at a pH less than 2.0.

12. The method as defined in Claim 11 wherein the step (d) is carried out at 95°C, for 2 hours, with 40 gpl free H_2SO_4 solution. (pH=0.1)

13. The method as defined in Claim 7 wherein in the step (e), the solid residue is washed with hot water or hot dilute sulphuric acid and the thus-obtained solution is combined with the strong acid leach filtrate before recycling into the fluidized bed reactor.

14. The method as defined in Claim 13 wherein the amount of said hot water or hot dilute sulphuric acid solution is twice the volume of the entrapped solution in the solid residue or less.

15. The method as defined in Claim 13 or 14 wherein hot water or hot dilute sulphuric acid solution over 90°C is used.

16. The method as defined in any one of Claims 7 to 14 wherein off gas from the fluidized bed reactor is fed to a H_2SO_4 plant.

17. The method as defined in any one of Claims 7 to 14 wherein zinc and copper are recovered.

18. The method as defined in any one of Claims 7 to 14 wherein zinc is recovered.

19. The method as defined in Claim 7 wherein

calcine from a dead roaster is continuously combined with the calcine from the fluidized bed sulphation reactor prior to the step (b).

20. The method as defined in Claim 7 wherein
5 calcines from a dead roaster are leached in separate trains or in semi-separate circuits, with the final strong acid leach solution being recycled to the sulphation roaster.

21. The method as defined in Claim 20
10 wherein the calcines from a dead roaster and the sulphation roaster are leached separately as in Claim 7, Step (b) and the leach pulps subjected to separate liquid-solid separation as in Step (c), the solid residue from the liquid-solid separation
15 from the sulphation roaster is subjected to leaching as in Step (d) the resultant pulp is subjected to liquid-solid separation as in Step (e), the resultant solution added to the solid cake produced from the dead roast leach pulp from
20 Step (c), the resultant pulp is subjected to leaching as in Step (d), the resultant pulp is thermally decomposed in the sulphation roaster as in Step (f).

22. The method as defined in Claim 19, 20 or
25 21, wherein the feed ratio to the fluidized bed sulphation reactor/dead roaster is determined in such a manner that the fluidized bed sulphation reactor becomes thermally autogeneous.

23. The method as defined in Claim 19, 20 or
30 21 wherein the sulphation roaster is not thermally autogeneous and fueling of the reactor is required.

24. The method as defined in Claims 19 to 23 wherein zinc and copper are recovered.

- 35 25. The method as defined in Claims 19 to 23 wherein zinc is recovered.

26. The method as defined in Claim 1 wherein
40 the strong sulphuric acid solution containing said metal and iron as sulphates is obtained by leaching any metal containing material with

strong sulphuric acid solution, said metal containing solution is decomposed in a fluidized bed reactor containing inert solid particles, said inert solid particles and pellets formed from
45 decomposed strong acid solution overflow from the fluidized bed reactor and are subjected to a water or dilute sulphuric acid leach, said inert solid particles are recycled to the reactor after separating the same from the pulp obtained after
50 the said leach.

27. The method as defined in Claim 1 wherein the strong sulphuric acid solution contains said metal and iron as sulphates is obtained by
55 leaching the final solid residue of a dead roasting process with strong sulphuric acid solution, the resulting pulp from the said strong acid leach is decomposed in said fluidized bed reactor, said reactor contains inert solid particles, and pellets formed from decomposed said pulp, the overflow
60 from the fluidized bed reactor is subjected to a water or dilute sulphuric acid leach, and said inert particles are recycled to the reactor after separating the same from the pulp obtained in said water or dilute leach.

- 65 28. The method as defined in Claim 27 wherein off gas from the dead roaster is fed to the fluidized sand bed reactor.

29. The method as defined in Claims 26 and 27 wherein the inert solid particles have a size
70 range between about No. 140 to No. 10 (105 μm to 2000 μm) in the U.S. standard sieve series.

30. The method as defined in any one of Claims 26 to 29 wherein said inert solid particles are silica sand.

- 75 31. The method as defined in any one of Claims 26 to 29 wherein zinc and copper are recovered.

32. The method as defined in any one of Claims 26 to 29 wherein zinc is recovered.